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QUANTITATIVE RADIOCHEMICAL DETERMINATION OF NICKEL-63 IN SEAWATER

by

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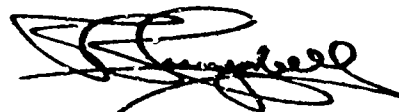R. Cole, Head

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ABSTRACT

A liquid scintillation method for the quantitative determination of Ni^{63} in seawater is described. The method consists in complexing the nickel in seawater with dimethylglyoxime, extracting it into chloroform, and then back-extracting the nickel into an aqueous phase using dilute sulfuric acid. An aliquot of this sample is added to a scintillation solvent and counted in a liquid scintillation counter.

SUMMARY

A rapid method for determining Ni^{63} in seawater has been developed. This method will be used for studying the corrosion of SNAP fuel encapsulant materials, using neutron activation analysis. In this procedure a sample of the nickel alloy encapsulant material is irradiated to produce the beta-emitting product nuclide Ni^{63}. The activated alloy is then placed in the corroding seawater medium. Periodically the seawater is drained from the sample chamber and the concentration of Ni^{63} is determined. The rate of corrosion of the alloy sample is then calculated from the rate at which its principal constituent, Ni, is released.

INTRODUCTION

A radiochemical procedure for measuring Ni^{63} in seawater was needed for determining accurately, in a short-term study, the rate of corrosion in seawater of a nickel alloy used to encase radioactive fuels in SNAP (Space Nuclear Auxiliary Power) reactors.

BACKGROUND

Corrosion-resistant materials are used for encasing radionuclide fuels to prevent, in an accident situation, the leakage of radioactive materials to the environment.

Several types of fuels being considered have long half-lives, in the order of a hundred years. A major environment in which these fuels might be immersed in case of an accident is the ocean. In this case, the container would have to maintain its integrity for many hundreds of years. However, predicting the long-term resistance of a suitable material requires highly accurate short-term measurement of its corrosion rate. Present measurement methods, for example differential weighing techniques, have proved generally unsatisfactory. The problem involved here is twofold: 1. There is difficulty in detecting the extremely small weight loss due to corrosion of the specimen, 2. the accumulation of organic or other matter requires abrasive cleaning of the sample before final reweighing; this may cause some damage to the surface and consequently interfere with the differential weighing technique.

OBJECTIVE

A program has been initiated at the U. S. Naval Radiological Defense Laboratory to attempt to refine the measurement technique so as to be able

to obtain accurate, short-term data on corrosion rates of a number of highly corrosion-resistant encapsulant materials. One alloy presently being studied is Hastelloy C, a metal composed of $\sim$ 57 % Ni, 16 % Cr, 17 % Mo, 4 % W and 5 % Fe. The metal sample is to be irradiated with thermal neutrons and the rate of corrosion is to be followed by measuring the activities (primarily of Ni^{63}) of the radioactive products leached into the seawater solution.

APPROACH

Ni^{63} is a beta-emitting isotope with a half-life of 92 years. Since the highest energy radiation associated with the nuclide is a 67-Kev beta-ray, difficulty is encountered in the ordinary counting techniques requiring solid sources. Self-absorption reduces the counting efficiency of solid samples and makes the interpretation of the data difficult. Gaseous samples, such as nickel carbonyl, on the other hand, present difficult problems of handling and system decontamination. For these and other reasons, a liquid-scintillation counting technique seemed the most promising approach. A previously reported study[1] had demonstrated the feasibility of the liquid-scintillation counting of Ni^{63}.

In the technique devised here, Ni^{63} activity in seawater is chelated with dimethylglyoxime. The activity is concentrated by extraction with a small volume of chloroform. The sample is then prepared for counting by back-extraction into an aqueous medium.

Since a high concentration of Ni in the final scintillator solution acts as a quenching agent, the operations are performed without the addition of nickel carrier. Consequently, quantitative removal of the nickel activity is required.

EXPERIMENTAL

MATERIALS

All chemicals used were ACS Reagent Grade.

Scintillator Solution: The scintillator solution contained 10 g of 2,5-diphenyloxazole (PPO) and 0.25 g of 1,4-bis-2(4-methyl-5-phenyloxa-zoly)-benzene (dimethyl POPOP) dissolved in toluene to make one liter of solution. The solution was stored in an amber bottle in the dark.

Standard Solutions: A secondary standard of Ni^{63} in dilute hydro-chloric acid was obtained from the Oak Ridge National Laboratory. The radiochemical purity was certified to be 99 %. Its specific activity was 1.57×10^5 dpm/µg Ni. This solution was check-calibrated against an intercalibrated[2] primary standard obtained from the Atomic Weapons Research Establishment, Aldermaston, Berkeshire, England. Aliquots of the second-ary standard were used throughout in the experimental procedure.

Tracers: The radioactive tracers were used in the form furnished by Oak Ridge National Laboratory.

APPARATUS

The counting system used was a Tri-Carb liquid scintillation spectro-meter, Model 314-A (Packard Instrument Co., La Grange, Ill.). The freezer section was maintained at $0^{\circ}C$.

Samples were counted in 22-ml screw-capped vials.

The counting instrument was calibrated to optimum settings of window width and high voltage using the Ni^{63} secondary standard. First, optimum high-voltage settings were determined at a fixed window width. Then op-timum window settings were obtained at a fixed optimum high-voltage set-ting. The final conditions chosen were a high-voltage tap setting of 4.5 and a window-width setting of 6.00. Background at these settings averaged 20 ± 2 cpm.

Counter efficiency was established by diluting the Ni^{63} primary standard so that 1 ml of the final solution contained 6.80×10^4 dpm. One-ml aliquots were placed in counting vials and the scintillator solu-tion was added. The average measured counting rate was $1.66 \pm 0.01 \times 10^4$ cpm, or a detection efficiency of 24.5 ± 0.15 %.

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PROCEDURE

Place 100 ml of seawater sample containing the Ni^{63} activity into a separatory funnel. Add 0.5 ml of an ethanolic solution of dimethylglyoxime (1 %). Mix the solution thoroughly and allow to stand for at least 10 min. Extract the nickel dimethylglyoxime by shaking with 10 ml of chloroform for 2-3 min. Drain the organic phase into another separatory funnel. Then wash the aqueous phase with 10 ml of chloroform and combine the organic extracts. Discard the aqueous phase. Back-extract the nickel into an aqueous phase by adding 10 ml of 0.1 N sulfuric acid and shaking for 1-2 min. Drain the organic phase into a clean separatory funnel and the aqueous phase into a 50-ml teflon beaker. Wash the organic phase with 10 ml of 0.01 N sulfuric acid. Discard the organic phase. Combine the aqueous phase with the previous one in the teflon beaker. Evaporate the solution to approximately 3 ml. Transfer quantitatively into a 5-ml volumetric flask and dilute to the mark with water rinses of the teflon beaker. Pipet 1 ml of the solution into a vial containing 10 ml of scintillator solution and 10 ml of ethanol. Mix the system thoroughly. Place the sample in the refrigeration chamber of the counter for 30 min before measuring its activity.

PROCEDURE DEVELOPMENT

In the development of this procedure for the determination of Ni^{63} in seawater, two groups of parameters were investigated.

The first comprised those factors that affected the counting rate of the liquid scintillation sample: concentrations of scintillators, aqueous volume, linearity of counting, reproducibility of counting, temperature, acidity, and stability of the counting sample.

The second comprised those factors concerned with the extraction of the nickel activity from the seawater: concentration of dimethylglyoxime reagent, pH of the seawater solution, recovery factors, back-extraction, and extraction of possible interfering radionuclides.

PARAMETERS AFFECTING COUNTING RATE OF LIQUID SCINTILLATION SAMPLES

Concentrations of Scintillators

To determine the optimum concentrations of the primary and secondary scintillators, identical radioactive samples containing varying amounts of scintillators were prepared and counted. The results indicated that a PPO concentration of 10 g per liter of toluene and a POPOP concentration of 0.25 g per liter of toluene would be satisfactory (Fig. _).

Effect of Aqueous Volume

Since liquid scintillation systems generally do not tolerate large volumes of aqueous solution, it was necessary to study the volume limits of samples being used in the toluene-ethanol system. In this study 0.5 to 1.8 ml of solution containing known, identical amounts of Ni^{63} were mixed with 20 ml of the scintillator-ethanol solution and counted. The results are presented in Table I. It appeared that if aqueous solution aliquots of larger than 1.2 ml were added to the scintillator solution there would be a decrease in the total number of observed counts. A part of the decrease in counting rate was probably due to some effect caused by the dilution of the scintillator as the aqueous volume increased. The aqueous aliquot volume was therefore set at 1 ml.

Linearity of Counting with Increased Concentration of Ni^{63}

To determine the linearity of counting ratio with varying activity levels, standard solutions containing varying amounts of Ni^{63} were prepared. One-ml aliquots of each solution were added to 20 ml of the scintillator-ethanol solution and counted. The results (Fig. 2) indicate a linear relationship between the true and observed counting rate over a wide range of activities. Counting errors were less than 1 %.

Reproducibility

To study the reproducibility of sample preparation, five identical Ni^{63} samples were individually prepared and counted. The results are given in Table II. The reproducibility of this method appears to be excellent.

Effect of Temperature

The effect of temperature on the counting rate was determined by measuring counting rate as a function of elapsed time after the sample
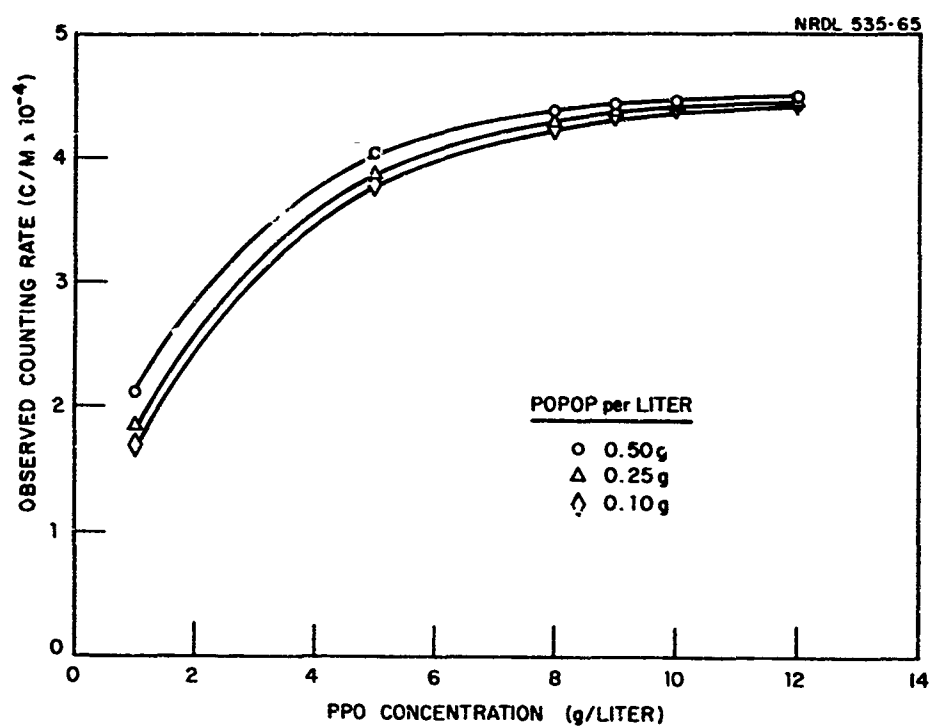
Fig. 1 Effect of Concentration of Scintillators on Counting Rate

TABLE I

Effect of Aqueous Volume

Aqueous Volume (ml)	Loss in Counting Rate ($\%$)[a]
0.5	0.0
1.0	0.0
1.2	0.2
1.3	0.8
1.4	1.8
1.5	3.0
1.6	3.2
1.7	3.4
1.8	3.5

a. Compared to aqueous volume of 1 ml.

TABLE II

Reproducibility of the Method

Sample Number	Observed Counting Rate (c/m)
1	178,100
2	178,598
3	177,851
4	177,643
5	179,246
Average	178,287 ± 576

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NRDL 535-65
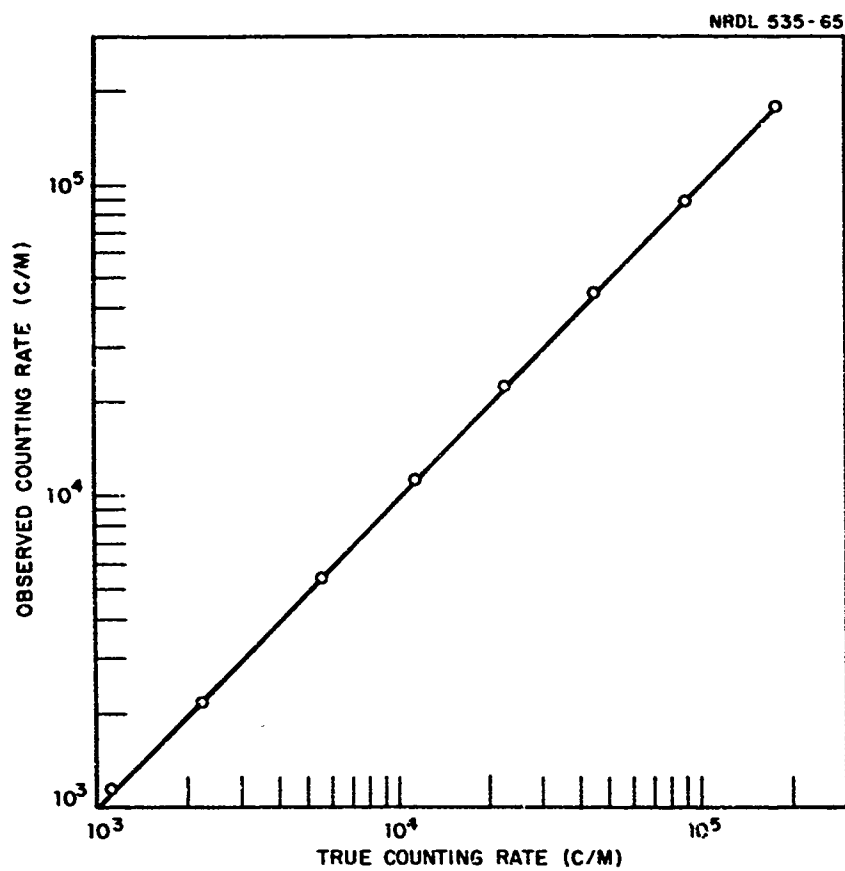
Fig. 2 Linearity of Counting Ni[63]

TABLE III

Effect of Temperature on Counting Rate

Time in Counter (min)	Counting Rate (c/m)
1	172,692
5	174,200
10	176,849
15	177,105
20	178,094
30	178,210
60	178,150

was placed in the freezer compartment of the counter at $0^{\circ}C$. A standard Ni^{63} solution was freshly prepared and immediately placed in the freezer compartment. Counts were taken at various intervals. Table III shows that a steady-state counting rate was reached and maintained after 20 minutes.

Effect of Acidity

To determine the effect of acid concentration on the counting rate, one-ml aliquots of Ni^{63} solution containing varying quantities of sulfuric acid* were mixed with 20 ml of the scintillator-ethanol solution and counted. The results (Table IV) show that the counting decreases as the acidity increases. The system would tolerate 1.5 N sulfuric acid with approximately 1 % loss in counting rate. Solutions with high acidity tended to decompose the scintillator, thus decreasing the counting efficiency. However, as can be seen in the following section, "Stability of Sample," a minimal acid concentration is necessary for maintaining the stability of the counting sample.

Stability of Sample

In order to assess the effect of pH on the stability of the samples, samples of various pH were prepared and stored in the dark at room temperature for varying periods of time up to 6 days. The results (Table V) demonstrated that solutions of 0.1 N HCl were stable for more than 6 days, while the counting rate of the other solutions (pH 5-6.5) gradually decreased. In solutions of low acidity, nickel was probably adsorbed

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*Sulfuric acid solution, described in the later section "Back-Extraction," is required to back-extract nickel into the aqueous phase.

TABLE IV

Effect of Acid Concentration

H_2SO_4 conc (normality)	Loss in Counting Rate (%)
0.5	0
1.0	0.6
1.5	1.1
2.0	3.6
3.0	6.3
5.0	9.9

TABLE V

Stability of Samples

Storage Time (days)	Counting Rate (c/m)	
	pH 1	pH 6
0	178,240	178,260
0.08	178,150	177,451
0.17	178,522	178,508
0.25	178,010	178,462
1.0	178,241	175,431
2.0	178,019	172,614
3.0	178,105	170,010
6.0	178,005	168,540

TABLE VI

Effect of pH on Extraction of Nickel From Seawater

pH	Percent Extracted
2.0	0.0
4.0	0.0
6.0	17.3
7.0	96.8
7.5	99.4
8.0	99.5
9.0	99.3

onto the walls of the liquid-scintillation counting vials, thereby resulting in 2π geometry and the consequent reduced counting efficiency.

PARAMETERS CONCERNED WITH THE QUANTITATIVE RECOVERY OF NICKEL FROM SEAWATER

Concentration of Dimethylglyoxime for Extraction

To determine the optimum concentration of the organic reagent, varying amounts of 1 % solution of dimethylglyoxime were used for the extraction. The recovery was essentially 100 % within the range investigated (0.1 to 5 ml DMG per 100 ml seawater).

Effect of pH on Extraction

Extraction of nickel from seawater solutions of varying pH was investigated. The results shown in Table VI indicate that quantitative recovery was not obtained from solutions of pH less than 7.5. Since the pH of natural seawater generally lies between 7.5 and 8.5, no further adjustment of pH is necessary for the extraction procedure.

Recovery of Ni by Dimethylglyoxime Extraction

The recovery of Ni from Dimethylglyoxime was studied. Table VII gives recovery values of Ni[63] found in the two organic phases and the one residual aqueous phase of a typical extraction. The initial mixing time was 3 min, but a time study showed that an interval of 2 min is sufficient for quantitative recoveries.

TABLE VII

Extraction of Ni[63] with Dimethylglyoxime in Chloroform
From Seawater (Seawater, 100 ml; DMG, 0.5 ml; Chloroform, 10 ml)

	Extraction Time (min)	Ni[63] Recovered (%)
CHCl$_3$ extract 1	3	97.7
CHCl$_3$ extract 2	2	2.1
Residual Aqueous Phase		0.3
	Total	100.1

Back-Extraction

Since chloroform acts as a quenching agent in liquid scintillation counting, it was necessary to back-extract nickel into an aqueous phase. This was easily done with acid solutions. However, since the scintillator solution could not tolerate a high acid concentration, it was necessary to determine the acid conditions for stripping that would not cause interference in the final counting sample. In this experiment a series of chloroform extracts containing Ni[63] were back-extracted with 10-ml portions of solutions of varying concentrations of sulfuric acid. The results (Table VIII) indicated that nickel could be back-extracted from the organic phase with 10 ml of 0.1 N sulfuric acid. This acid concentration was compatible with the final counting conditions.

TABLE VIII

Back-Extraction of Nickel From Organic Phase Into
Aqueous Phase

H$_2$SO$_4$ Concentration (normality)	Percent Stripped
0.035	84.1
0.070	94.0
0.108	100.0
0.140	100.0
0.180	100.0

Extraction of Other Radionuclides

When the SNAP metal samples are initially irradiated with neutrons, other radionuclides besides Ni^{63} are produced. These may include:

Fe-58 (n,γ) Fe-59
Mo-98 (n,γ) Mo-99
W-184 (n,γ) W-185
Cr-50 (n,γ) Cr-51
Ni-58 (n,p) Co-58
Ni-60 (n,p) Co-60
Fe-54 (n,p) Mn-54

In studying the corrosion behavior of the metal in seawater, then, activities other than Ni^{63} will be found. Consequently it was necessary to determine whether these other activities would interfere with the Ni analysis. This was done by studying the extractability of these radionuclides into dimethylglyoxime-chloroform and the stripping with 0.1 N sulfuric acid. The amount of each radionuclide recovered finally in the stripped aqueous phase is given in Table IX. Among the nuclides tested, none showed any significant interference with the nickel extraction. The data indicated that a minimum decontamination factor of approximately 10^3 can be achieved by the foregoing procedure.

TABLE IX

Extraction of Elements with 0.1 % DMG in $CHCl_3$ From Seawater

Nuclide	Percent Extracted
Fe-59 (III)	0.13
Co-60 (II)	0.17
Mn-54 (II)	0.09
Cr-51 (III)	0.17
W-184 (VI)	< 0.01
Mo-99 (VI)	< 0.01

RESULTS FROM A SERIES OF SAMPLE ANALYSES

To demonstrate the accuracy and precision of the above procedure a series of seven 100-ml seawater samples, to which were added from 5.0×10^2 c/m to 1.75×10^6 c/m of Ni^{63}, were analyzed. The results are shown in Table X. The average recovery was 99 %, with a standard deviation of 0.94 %. The small loss probably was due to incomplete transfer of the separated phases during the extraction procedure. For samples of very low nickel activity, increased sensitivity could be obtained by either using larger seawater samples or by evaporating the final aqueous volume to 1 ml in the counting vial.

TABLE X

Recovery of Nickel^{63} From Seawater

Ni^{63} Added (c/m)	Ni^{63} Recovered (%)
5.00×10^2	97.8
1.00×10^3	98.5
1.70×10^3	101.5
6.79×10^3	99.1
6.79×10^4	98.4
1.75×10^5	98.1
1.75×10^6	99.4
Average	99.0 ± 0.94 %

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A liquid scintillation method for the quantitative determination of Ni^{63} in seawater is described. The method consists in complexing the nickel in seawater with dimethylglyoxime, extracting it into chloroform, and then back-extracting the nickel into an aqueous phase using dilute sulfuric acid. An aliquot of this sample is added to a scintillation solvent and counted in a liquid scintillation counter.

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